Prediction by near infrared spectroscopy of the biochemical composition of various raw materials used in the organic fertiliser industry

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Introduction

Added organic materials [1], composts and organic fertilisers are involved in building soil organic matter. They are a factor in soil property improvement, and can represent an important source of nutrients for both plants and soil organisms. Even a century ago [2], the composition of added organic materials was thought to have a direct influence on organic matter transformation. Intense work is still devoted to investigating the relationships between the characteristics and the transformations of added organic materials [3]. The fibre content, estimated by Van Soest fractions [4], proved to be a good indicator of the potential capacity of carbon and nitrogen transformations [5 - 11].

The nature and characteristics of composts and organic fertilisers can vary in a large range as they may originate from very different sources of raw materials such as tofu refuse [12], municipal wastes [13], mixtures of manure and vegetables [14] and manures for mushroom growing [15 - 16]. Their elaboration may also vary according to producers.

In order to evaluate the ability of organic fertilisers to induce carbon and nitrogen transformations when added to soils, we have previously investigated the relationships between their characteristics and their transformations [7, 8, 11]. Nevertheless, a complete fibre analysis which involves five different fractions is expensive and time-consuming.

Hence a programme was set up to evaluate the potential of using near infrared (NIR) spectroscopy to assess the quality of raw materials used in compost and organic fertilisers.

Materials and methods

Organic materials

A total of 706 samples were chosen in order to encompass a wide variability. The raw materials originated from (i) industrially pre-processed plant residues, principally collected in the largest organic fertiliser factory in France or from other sources: wet and dry grape skins, de-oiled grape pips, coffee cake, de-fatted cocoa bean, cocoa skin, olive pulp, maize cob, barley straw, rice hulls, rapeseed cake, soybean cake; and (ii) tropical plant residues samples collected from the field in Brazil and Kenya, as parts of trees, shrubs, crops, cover crops, used in a framework of research studies on mitigation of green house gas emissions. These tropical organic materials covered several plant parts including total above ground material, roots, stems, twigs, pods, leaves and litters, and were all potentially utilisable in composting.

Sample preparation and reference analyses

Each sample was analyzed for its moisture content by drying to constant weight in an oven at 105°C. Subsets of samples were measured for organic matter (OM) content by subtracting the ash content (weight remaining after ignition at 525°C over night) from the original weight of sample, and for total nitrogen (N) content (Kjeldahl method). Due to the heterogeneity of fresh materials, all the samples were dried (40°C) and ground to pass through a 1-mm sieve for a sequential analysis of fibre content [17]. Each ground organic material sample was successively extracted for neutral detergent fibre, acid detergent fibre and acid detergent lignin. The acid detergent lignin was thus determined on acid detergent fibre which was in-turn determined from the neutral detergent fibre. At each extraction step, the products obtained were filtered, dried at 40°C, weighed, and one replicate dried at 105°C dried for determining residual moisture, then ignited gradually at 525°C for ash content. Each fraction was calculated on an ash free basis. The fibre parameter considered in this study was acid detergent lignin. No samples were measured for all three parameters of organic matter, total nitrogen or lignin content.

Sample scanning and data analysis

Each of the 706 samples was scanned on a NIRS 6500 (Foss NIRSystems, Silver Spring, MD, USA) in duplicate in ring cups. Spectral data were collected every 2 nm from 400 to 2,498 nm. Individual spectra, each consisting in 32 scans, were stored as log (1/R) using a ceramic standard reference spectrum. The spectra were corrected with a standard normal variate and detrend (2,5,5) (Win-ISI, Infrasoft International, Port Matilda, PA, USA) mathematical treatment [18]. Visible wavelengths were discarded as they introduced instability in the models. Calibrations of the parameters studied here were performed using a modified partial least square regression WIN-ISI, Infrasoft International, Port Matilda, PA, USA) [19], The standard error of calibration, the coefficient of determination , and the standard error of cross-validation were calculated. In order to minimize over-fitting of the equations, cross-validation was used as an internal validation during calibration development.

Results and discussion

All the parameters varied widely (Table 1) because of the diversity of the raw materials. Although of plant origin, the materials encompassed a wide diversity of plant parts and species from very different geographical and climatic origins. Most of the materials entering the agro-food industry differ from those collected from the field, and, as they are more or less transformed by industrial processes such as extractions and fermentations, resembled fresh manures or composts in the early stages of processing. Therefore NIR spectroscopic predictions developed here differ from those dedicated to crop residues [20, 21], tropical plant parts and litters [22], or Mediterranean shrubs and tree origins alone [23 - 25]. Our predictions encompass this variability.

Table 1. Performance of calibration models for lignin, organic matter and total nitrogen content of samples of a range of organic materials suitable for composting.

Constituent ($g \cdot 100g^{-1}$ dry weight)	Population			Calibration statistics			
	n	Mean	SD	SEC	R^2	SECV	RPD
Lignin	124	28.1	16.0	3.03	0.96	3.51	4.6
Organic matter	317	93.2	2.99	0.78	0.93	0.97	3.1
Total nitrogen	271	2.3	0.54	0.16	0.92	0.18	3.0

SD: standard deviation of parameter in the population

SEC: standard error of calibration

R^2: coefficient of determination of calibration

SECV: standard error of cross-validation

RPD: ratio of performance to deviation ($SD.SECV^{-1}$)

The models developed for the three parameters of organic matter, total N and lignin content were accurate, as their determination coefficients equalled or exceeded 0.92, and the ratio of the standard deviation to the standard error of cross-validation were all equal or above 3. The highest standard error of calibration was associated with lignin content. This is not surprising, as the lignin fraction is the last one obtained during the sequential analyse of fibres. The estimates of lignin content therefore include small experimental errors accumulated along the entire sequence. The standard error of cross-validation varied in a rather similar trend (from 0.18 to 3.51 g $100g^{-1}$ dry weight), compared to standard error of calibration (from 0.16 to 3.03 g $100g^{-1}$ dry weight). With the standard error of cross-validation being close to their corresponding standard error of calibration, the models could be considered as robust.

Predictions of lignin content, OM and total N were compared to their corresponding reference data (Figure 1). The agreement was particularly good for lignin content. Dispersion was more noticeable for OM and total N, with some outlier values. The dispersion observed for the low values of OM could be explained by the presence of soil contaminating these litter samples, and associated potential problems when filling the ring cups. For total N, the outliers values may have been due to the reference measurement or to the calibration on account of the different natures of the samples, or the lack of a sufficient number of samples with total N values exceeding 3 g $100g^{-1}$ dry weight, compared to the numerous samples with total N values between 2 and 3 g $100g^{-1}$ dry weight.

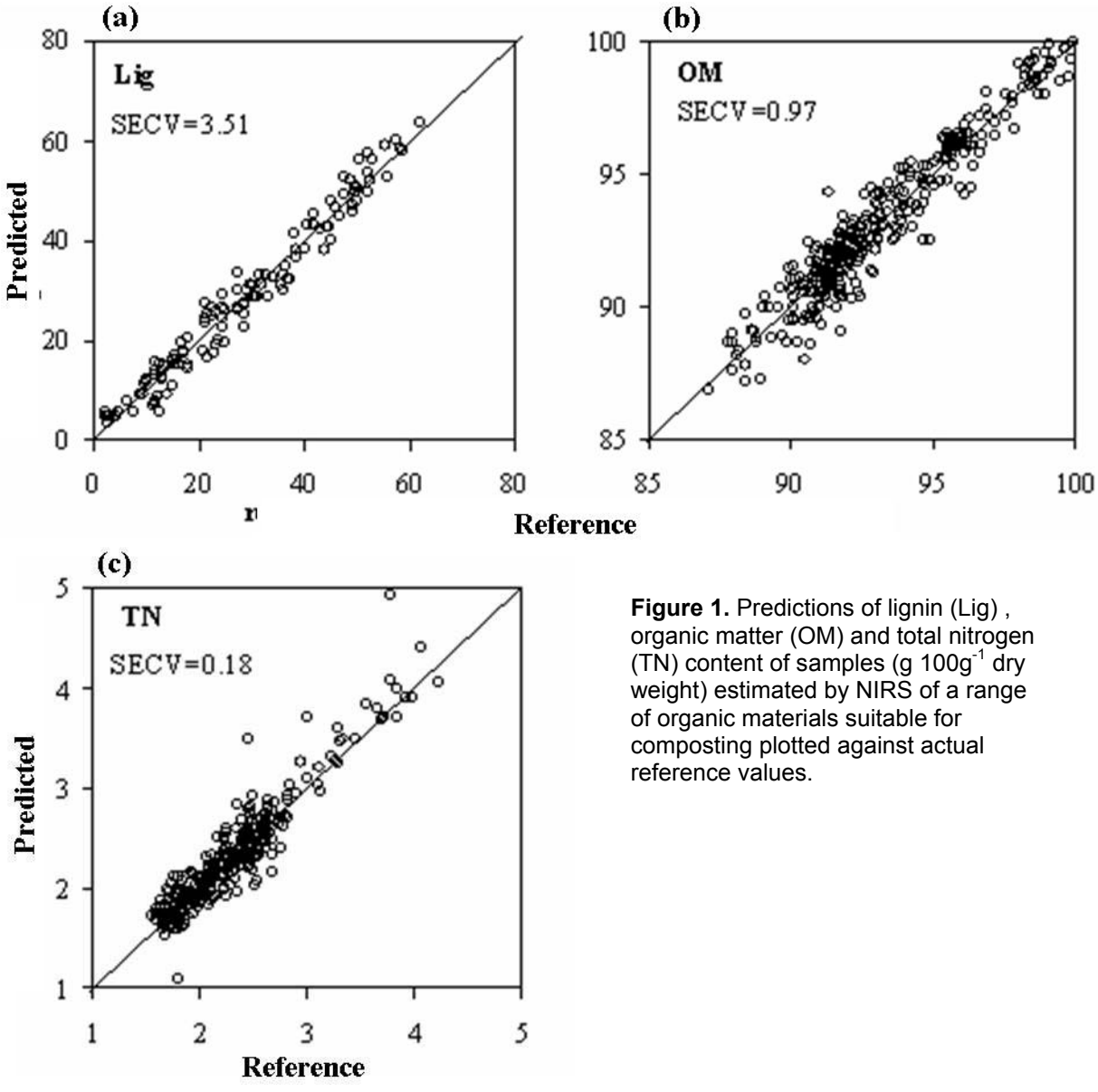

Figure 1. Predictions of lignin (Lig) , organic matter (OM) and total nitrogen (TN) content of samples (g $100g^{-1}$ dry weight) estimated by NIRS of a range of organic materials suitable for composting plotted against actual reference values.

The precision of the developed models was satisfactory (Figure 2). This was particularly true for OM, with its standard error of cross-validation being equal to the standard error of the reference method. Even though the standard error of cross-validation for total N was three times the standard error of the reference method the estimated value was itself low (0.18 $100g^{-1}$ dry weight). As lignin is the final fraction obtained during the analytical sequence for the extraction of fibres, its standard error of cross-validation was twice the standard error of the reference method which is also a good result. Considering the cost and time required to obtain this fraction, the precision of the NIR spectroscopy prediction was adequate to rank the quality of raw materials used in compost. Furthermore, the standard error was lower than the normative tolerances (maximum 3.0 g $100g^{-1}$ bulk weight for OM, and range from minimum to maximum of 0.2 to 0.3 g $100g^{-1}$ bulk weight for total N) for organic soil improvers (French standard NFU 44-051 [26]).

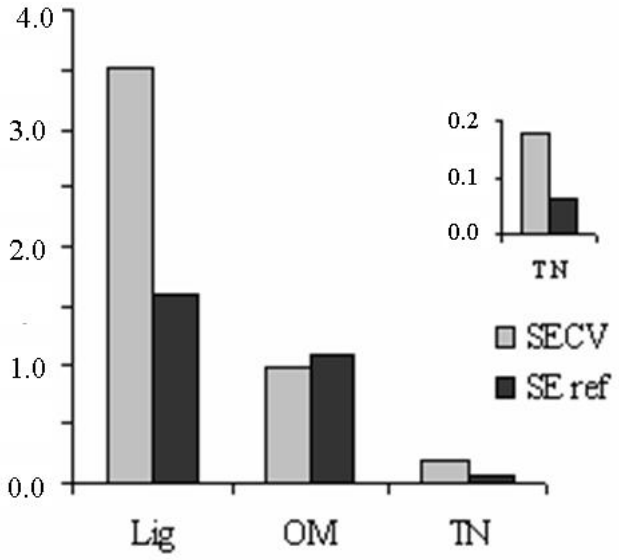

Figure 2. Standard error of reference data (SE ref) plotted with the standard error of cross-validation (SECV) using NIR spectroscopy for lignin, organic matter and total nitrogen content of a range of organic materials suitable for composting.

Conclusions

The precision of the models obtained has been shown to be suitable for a global characterisation of samples. It was concluded that the major parameters used in quality characterisation of raw materials used in compost and organic fertilisers can be estimated by NIR spectroscopy with sufficient accuracy that the procedure can be applied to routine quality control.

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